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Spin Obit Interaction

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The spin-orbit interaction

P. A. M. Dirac published a relativistic, quantum mechanical description of electrons in 1928. The description contained several effects not present in Schrödinger's wave mechanical description of electrons: the electron has an intrinsic spin, a component of the total angular momentum of an atom or molecule; there is a magnetic moment associated with the spin; there in an interaction between this magnetic moment and the orbital angular momentum of the electron.

The suggestion that an electron is a spin-$\frac{1}{2}$ particle had been advanced in 1925 to explain spectroscopic observations that had been made of alkali metal atoms. In 1927 Pauli had constructed a quantum mechanical description of this angular momentum. The magnitude of the associated magnetic moment had also been deduced by spectroscopists. So the only revelation in Dirac's argument was (1°) the recognition of the close connection between spin and special relativity and (2°) the deduction of an explicit expression for the spin-orbit coupling. I think Dirac's argument* for all this is the most natural, but the requisite familiarity with special relativity made Dirac's argument unpopular with textbook writers. More often, textbooks try to "rationalize" the spin-orbit coupling term as an accumulation of simple "well known" effects. One person's "well known" is another's "mystically obscure." I present here the conventional argument with my interpolations of what is "well known."

* P. A. M. Dirac, *Proc. Royal Soc. (London)* **117 A**, 610 (1928).

A. Coulomb Interactions in Molecules

1. Coulomb interactions felt by electrons

The electron has a charge $-e \Rightarrow$ there are Coulomb forces between all electrons and between each electron and the nuclei in a molecule. These are the largest forces on electrons in atoms and molecules. The associated electrostatic energy depends on the positions of all the electrons $\{\boldsymbol{r}_i\}_{i=1}^{N}$:

$$-\frac{e^2}{4\pi\epsilon_0}\sum_{\substack{i=1,\ldots N\\ \text{nuclei } I}}\frac{Z_I}{|\boldsymbol{R}_I-\boldsymbol{r}_i|}+\frac{e^2}{4\pi\epsilon_0}\sum_{1\le i<j\le N}\frac{1}{|\boldsymbol{r}_j-\boldsymbol{r}_i|} \qquad (1,\ SI\ units)$$

The expression (1) is *invariant* under *all* spatial rotations in 3D. A rotation in 3D induces a unitary transformation of the state of a system. It was well known to the creaters of quantum mechanics (see Appendix L) that such transformations are generated by an Hermitian operator. Feynman (see the cited reference), shows how to identify this operator:

(a) If the rotation takes

$$\boldsymbol{r}\rightarrow\boldsymbol{r}+\boldsymbol{r}\times\delta\vec{\phi}$$

with $\delta\vec{\phi}$ a vector (1) of length=the angle of rotation and (2) with direction =the axis of rotation, then this rotation maps any function of $\boldsymbol{r}$

$$\begin{aligned} f(\boldsymbol{r})\rightarrow & f(\boldsymbol{r}+\boldsymbol{r}\times\delta\vec{\phi})=\sum_{n=0}^{\infty}\frac{1}{n!}\left[\boldsymbol{r}\times\delta\vec{\phi}\cdot\nabla\right]^n f(\boldsymbol{r})\\ &=\sum_{n=0}^{\infty}\frac{1}{n!}\left(\frac{i}{\hbar}\boldsymbol{r}\times\delta\vec{\phi}\cdot\hat{\boldsymbol{p}}\right)^n f(\boldsymbol{r})=\sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{i}{\hbar}\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}}\cdot\delta\vec{\phi}\right)^n f(\boldsymbol{r})\\ &=\sum_{n=0}^{\infty}\frac{1}{n!}\left(-\frac{i}{\hbar}\hat{\boldsymbol{L}}\cdot\delta\vec{\phi}\right)^n f(\boldsymbol{r})=e^{-\frac{i}{\hbar}\delta\vec{\phi}\cdot\hat{\boldsymbol{L}}}f(\boldsymbol{r}) \end{aligned} \qquad (2)$$

with $\hat{L}=\hat{\boldsymbol{r}}\times\hat{\boldsymbol{p}}$, the (orbital) angular momentum operator of the electron.

(b) Feynman also shows that the known way in which rotations in 3D about different axes fail to commute $\Rightarrow$ the $\hat{L}$'s associated with different axes fail to commute. He deduces that

$$[\hat{L}_x,\hat{L}_y]=i\hbar\hat{L}_z,\quad \textit{et cetera.}$$

The commutation relations among the components of $\hat{\vec{L}}$ are the commutation relations associated with angular momentum. The *generators* (2) of rotations in a system are simply the angular momenta operators of the system.

(c) Since rotations leave the Coulomb interactions invariant, $\vec{L}$ commutes with the Hamiltonian $\Rightarrow$ $\vec{L}$ is a conserved quantity and the angular momentum eigenfunctions will also be energy eigenfunctions. Energy eigenfunctions can be labeled with ℓ, m indices.

2. Maxwell's theory

Maxwell combined all the known relations between the electric field, the magnetic field, and matter into a coherent whole. One of the results was the recognition that light was an electromagnetic wave. He calculated the propagation speed c of the wave in terms of static electrical properties that had been measured in the laboratory, stimulating experiments to verify the theory.

As $c \gg$ the speed v of material particles, it is natural to order contributions to theories by how they scale with v/c. The expression (1) used for Coulomb forces corresponds to the $v/c \to 0$ limit of the predictions of Maxwell's theory. We say, the Coulomb forces are the only *non-relativistic* interactions involving electrons, the only iteractions that survive the $c \to \infty$ limit.

3. Lorentz's theory

The relations packaged by Maxwell distinguished contributions of "free charges, " and "bound charges" (naively, "external" charges and charges "induced" in dielectrics, ...). Creeping up on $\sim$ 1900, H. A. Lorentz reformulated this theory as a "theory of electrons," the first "elementary particle" theory. Not having two classes of charges gave a much simpler picture.

One of the formal questions addressed by Lorentz was how the appearance of the electromagnetic field depended on the observer's velocity. If, for example, you observe an electron moving by you with a velocity $\boldsymbol{v}$, you would see both an electric $\boldsymbol{E}$ (Coulomb) field and a magnetic $\boldsymbol{B}$ (Ampère) field. But, if you were also moving with $\boldsymbol{v}$, you would not see a magnetic field. In general, a rule that describes how properties change when one moves

from a non-moving "inertial frame" to a moving "inertial frame" is called a Lorentz transformation.

In the case of $\boldsymbol{E}$ and $\boldsymbol{B}$, the rules depend on whether one looks at the components of the vectors parallel ($\boldsymbol{E}_\parallel$, $\boldsymbol{B}_\parallel$) or perpendicular ($\boldsymbol{E}_\perp$, $\boldsymbol{B}_\perp$) to $\boldsymbol{v}$:

$$\begin{aligned}
\boldsymbol{E}_\parallel &\to \boldsymbol{E}_\parallel \\
\boldsymbol{B}_\parallel &\to \boldsymbol{B}_\parallel \\
\boldsymbol{E}_\perp &\to \frac{\boldsymbol{E}_\perp + \boldsymbol{v}\times\boldsymbol{B}_\perp}{\sqrt{1-v^2/c^2}} \\
\boldsymbol{B}_\perp &\to \frac{\boldsymbol{B}_\perp - \boldsymbol{v}\times\boldsymbol{E}_\perp/c^2}{\sqrt{1-v^2/c^2}}
\end{aligned} \tag{2}$$

4. Special relativity

According to Lorentz, if a light wave is reexamined in a moving frame, the frequency and wave length shift, but the propagation speed c is unaltered. Colloquially, c is invariant under all Lorentz transformations.

The accepted rules for mechanics, however, were not invariant under Lorentz transformations. In 1905 Einstein proposed a new formulation of mechanics that gave rules that were invariant under all Lorentz transformations. We now distinguish *relativistic* (Lorentz transform invariant) mechanics from *classical* mechanics (the $v/c \to 0$ limit of the relativistic rules, the original Newtonian rules).

5. Dirac's electron

In 1926 Schrödinger created a "wave mechanics" that identified the *energy levels* of the hydrogen atom. In his first attempt, he started from a relativistically (*i.e.*, a Lorentz transform) invariant description of mechanics, but the resulting "wave equation" didn't give the known energy levels for the hydrogen atom. In the end, he published a non-relativistic argument that did give the correct energy levels, implying that there would be *relativistic corrections* to Schrödinger's wave mechanics.

It was not until 1928 that a relativistically invariant wave mechanics was developed for electrons by P. A. M. Dirac. The key invention of Dirac was the replacement of the

image that the wave function was a simple field $\psi(\boldsymbol{r}, t)$ with the image that the quantum mechanical state function would be a *four-component* quantity, (a Dirac *spinor*, $\psi_i(\boldsymbol{r}, t)$, $i = 1, 2, 3, 4$, we say.) [Everything comes in fours in special relativity since "space-time" is four dimensional.]

New Hermitian operators (operators that intermix the components $\psi_i(\boldsymbol{r})$) appear in Dirac's theory. The generators for rotations of the $\psi_i(\boldsymbol{r})$, for example, are not simply the $\hat{\boldsymbol{L}}$, but they are $\hat{\boldsymbol{L}} + \hat{\boldsymbol{S}}$, with $\boldsymbol{S}$ the operator corresponding to the *intrinsic*† spin $(\hbar/2)$ of the electron ($\boldsymbol{S}$ mixes up the components $\psi_i(\boldsymbol{r})$ of the state function). The Dirac spinor describes both electrons and positrons. When the actual particle is an electron, two of the components are smaller than the other two by a factor $\sim v/c$. These are usually ignored by chemists, leading to the familiar two component picture of *spin*.

The commutation relations for the components of $\hat{\boldsymbol{S}}$ are the same as for the components of $\hat{\boldsymbol{L}}$, so the spin angular momenta behave like real angular momenta and the total angular momentum of a molecule is just the sum of all the separate orbital and spin angular momenta of the constituents.

B. The Electrical Interactions of electrons in a molecule

1. The Coulomb interaction

The Coulomb interactions between the electrons and nuclei in a molecule give rise to the term given in Eq.(1) in the Hamiltonian of a molecule.

2. The magnetic moment of the electron

There is a magnetic moment associated with the four component wave function.‡ In fact, the magnetic moment is proportional to the intrinsic angular momentum,

$$\hat{\boldsymbol{\mu}} = \gamma \hat{\boldsymbol{s}}/\hbar$$

† *Intrinsic* means that there is no picture of this property in terms of some internal structure of the electron. The electron is a *point particle* on all spatial scales. It is the introduction of the $\psi_i(\boldsymbol{r})$ components that gives rise to the *intrinsic* properties of the electron.

‡ Some details of this are summarized in Appendix W.

(with the gyromagnetic ratio $\gamma \approx e\hbar/m < 0$, $\approx$ twice the value associated with the orbital motion of electrons; $\hbar$ has been divided out in this expression to make the eigenvalues of $\hat{s}$ be dimensionless: the numbers $\pm\frac{1}{2}$.). $\boldsymbol{\mu}$ is the only electrical property that couples the intrinsic spin to the positions of the electrons, the $\{r_k\}$: If a magnetic field $\boldsymbol{B}(r)$ is present at the location r of the electron, there will be a Zeeman interaction term

$$-\boldsymbol{\mu} \cdot \boldsymbol{B}(r) \tag{3}$$

in the Hamiltonian.

There are four distinct sources of magnetic fields in a molecule that contribute terms of the form (3) to the Hamiltonian.

1° The orbital motion of the electrons gives rise to a magnetic field. An orbital motion with $\vec{L} \neq 0 \sim$ a circular current about the rotation axis. This gives rise to a magnetic moment $\gamma \vec{L}$ with $\gamma = \frac{e}{2m}$, the classical gyromagnetic ratio of electrodynamics. If

$$\mathcal{M}(r) = \left(\frac{3\, x_i\, x_j}{r^2} - \delta_{i\,j} \right)$$

is the dipole-dipole coupling tensor, the interactions of an electron with the orbital angular momentum is simply

$$-\hat{\mu} \cdot \frac{\mu_0}{4\pi |r - \boldsymbol{R}|^3} \mathcal{M}(r - \boldsymbol{R}) \cdot \gamma\, \vec{L} \qquad (4,\ SI\ Units)$$

if $\boldsymbol{R}$ locates the orbital angular momentum. Averaging over r leads to an interaction $\propto \vec{S} \cdot \vec{L}$.

2° The *nuclei* have magnetic moments $\boldsymbol{m}_I$ so there is a second magnetic dipole-magnetic dipole contribution to the energy of an electron located at r_i,

$$-\hat{\mu}_i \cdot \sum_{\text{nuclei } I} \frac{\mu_0}{4\pi |r_i - \boldsymbol{R}_I|^3} \mathcal{M}(r_i - \boldsymbol{R}_I) \cdot \vec{m}_I \qquad (5,\ SI\ Units)$$

3° The magnetic moments of the electrons make another magnetic dipole-magnetic dipole contribution to the electronic energy,

$$-\sum_{1 \leq i < j \leq N} \frac{\mu_0}{4\pi |r_i - r_j|^3} \hat{\mu}_i \cdot \mathcal{M}(r_i - r_j) \cdot \hat{\mu}_j \qquad (6,\ SI\ Units)$$

4° Although there is no magnetic field in the rest frame of the nucleus associated with the nuclear charge, Eq.(2) identifies a magnetic field

$$\boldsymbol{B} = -\frac{\boldsymbol{v} \times \boldsymbol{E}}{c^2\sqrt{1 - v^2/c^2}} \tag{7}$$

in the rest frame of an electron moving with velocity $\boldsymbol{v}$ through the electric field $\boldsymbol{E}$ of the nucleus. Identifying $\boldsymbol{v}$ with the linear momentum of the electron,

$$\boldsymbol{v} = \boldsymbol{p}/m \tag{8}$$

and recognizing that $\boldsymbol{E}$ is radial,

$$\boldsymbol{E} = \left|\frac{E}{r}\right| \boldsymbol{r} \tag{9}$$

we can rewrite (7)-(9) as

$$\boldsymbol{B} = \frac{\boldsymbol{r} \times \boldsymbol{p}}{m\,c^2\sqrt{1 - v^2/c^2}} \left|\frac{E}{r}\right| = \frac{\hat{\boldsymbol{L}}}{m\,c^2\sqrt{1 - v^2/c^2}} \left|\frac{E}{r}\right| \tag{10}$$

If $U(r)$ is the (radially symmetric) electrostatic potential associated with the nucleus,

$$|E| = \frac{\partial V}{\partial r} = \frac{1}{e}\frac{\partial U(r)}{\partial r} \tag{11}$$

and

$$\boldsymbol{B} = \frac{1}{m\,r\,e\,c^2\sqrt{1 - v^2/c^2}} \frac{\partial U(r)}{\partial r} \boldsymbol{L} \tag{12}$$

It is important to note at this point that $\boldsymbol{B}$ is a positive number multiplied by $\boldsymbol{L}$, meaning that the magnetic field is parallel to the orbital angular momentum of the particle. Using $\boldsymbol{\mu} = -\frac{e}{m\,c}\hat{\boldsymbol{s}}$,

$$\boldsymbol{\mu} \cdot \boldsymbol{B} = -\frac{\boldsymbol{s} \cdot \vec{L}}{m^2c^2\sqrt{1 - v^2/c^2}} \frac{U'(r)}{r} \tag{13}$$

There remains one additional relativistic effect. In introductory descriptions of special relativity, the idea of the *Lorentz contraction* is introduced: the length of an object that is moving with respect to the observer is "contracted" in the direction of the motion. This is not quite correct: If you are moving with respect to an object, some

of the light coming from behind the object can reach you since $c < \infty$. An object moving at a speed v doesn't appear "contracted," it appears rotated. In 1924, A.S. Eddington published in his book *The Mathematical Theory of Relativity* (Cambridge 1924) an argument by the cosmologist de Sitter that, if a spinning moon moves in an orbit around a planet, the motion around the planet contracts the spin angular momentum by $(1 - \sqrt{1 - v^2/c^2})$. L. H. Thomas did a similar calculation for an electron in 1926 and showed that the energy estimate in (12) was off by a factor of 2 because of this contraction. [That this "correction" was required had already been suggested by spectroscopists.] Adding the "Thomas $\frac{1}{2}$" leads to the assessment

$$\boldsymbol{\mu} \cdot \boldsymbol{B} = -\frac{\vec{s} \cdot \vec{L}}{2m^2c^2} \frac{U'(r)}{r} \tag{14}$$

for the spin-orbit interaction (well, the leading term in an expansion in v/c). This is the term that Dirac found in his relativistic description of electrons moving in external fields, although no similar term had appeared in previous attempts to provide a relativistic description of the electron.

The generalization to molecules is that there is a term

$$H_{SO} = \sum_{\text{electrons},i} \xi(r_i)\, \vec{L}_i \cdot \vec{S}_i \tag{15}$$

$$\text{with} \quad \xi(r_i) = \frac{1}{2m^2c^2\, r_i} \frac{dV_i(r_i)}{d\, r_i} \tag{16}$$

in the Hamiltonian for electrons in a molecule.

C. Atomic/Molecular Orbitals

To evaluate the interactions in (15), we must be able to associate electrons, i with *orbitals* with well defined $\vec{L}_i$ and $\vec{S}_i$. Such associations are routinely made by spectrocopists when they describe the states of multi-electron systems using the *aufbau* principle: The multi-electron system is pictured as possessing a set of one-electron states (orbitals) and the states of the system are found by placing the electrons in these *orbitals* with proper attention to the Pauli exclusion principle.

As the interactions between electrons in a multi-electron system are strong, it is incorrect to attribute to individual electrons an energy, a spin, or an orbital angular momentum. The *aufbau* principle is really just a *strategem* that requires a formal justification. A justification was provided by Paul Ehrenfest (at the University of Leiden): He introduced (from statistical mechanics) the idea of *adiabatic invariants*: If the Hamiltonian of a system is slowly "changed," what properties of a system remain unaltered? One property he identified was that an energy eigenstate of the Hamiltonian would remain an energy eigenstate under an adiabatic change of the Hamiltonian. This means that energy eigenstates of real systems can be (uniquely) associated with energy eigenstates with well defined $\vec{L}_i$ and $\vec{S}_i$ by simply (adiabatically) shutting off the electron-electron interactions. This means we can use $\vec{L}_i$ and $\vec{S}_i$ to label orbitals. Further, when the electron-electron interactions are shut off, it is easy to "find" the energy eigenstates so this picture also comes with familiar pictures of what the states look like.

As shown in §A.1, the rotational invariance of a molecule $\Rightarrow$ there is a conserved vector, the total angular momentum $\boldsymbol{J} \Rightarrow$ we can label angular momentum states with quantum numbers J, J_z. When the electrons don't interact, each orbital has quantum numbers $j_i, j_{z,i}$ that can be used to label the orbitals. The generalization of the argument in §A.1 to space-time rotations is that there is conserved vector, the total spin angular momentum $\boldsymbol{S}$. For the non-interacting electron system this $\Rightarrow$ each orbital has quantum numbers $s_i, s_{z,i}$.

In short, we first picture the molecule as consisting entirely of non-interacting electrons. The energy eigenstates correspond to orbitals with a well defined energy (labeled with a "principal quantum number" n), an "orbital angular momentum" labeled with ℓ, ℓ_z, and a "spin angular momentum" labeled with s,s_z ($\boldsymbol{j} = \boldsymbol{\ell} + \boldsymbol{s}$).

We then use the *aufbau* principle to construct multi-electron states for the system. Since, quantum mechanically, $\vec{\boldsymbol{j}}$ and $\vec{\boldsymbol{s}}$ behave like real angular momenta, this construction is mostly an exercise in the addition of angular momenta. Labeling the actual states of molecules depends upon *angular momenta addition rules* (or, in group theoretical jargon, on the irreducible representations of states of molecules that have multiple angular momenta components.) Teaching the use of these rules is the core quantum mechanical education of spectroscopists.

D. How big is the spin-orbit interaction?

We can get a quantitative estimate for the spin-orbit interaction term (14) by looking at the orbitals of electrons in atoms. If the electron-electron interactions are turned off, the states of an atom are simply the hydrogenic states associated with a nuclear charge $+Z\,e$, worked out in every introductory quantum mechanics text. For these states,

$$V_i(r) = -\frac{Z\,e^2}{4\pi\epsilon_0\,r} \quad \Rightarrow \quad \xi(r) = \frac{1}{2m^2c^2}\frac{Z\,e^2}{4\pi\epsilon_0}\frac{1}{r^3} \tag{17}$$

To estimate the spin-orbit interaction, we calculate

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{2Z^3}{a_0^3 n^3 l(l+1)(2l+1)} \tag{18}$$

for hydrogenic wavefunctions (here $a_0 = 4\pi\epsilon_0\hbar^2/m\,e^2$ is the Bohr radius).

As $\boldsymbol{J} = \boldsymbol{L} + \boldsymbol{S}$,

$$\boldsymbol{J}^2 = \boldsymbol{L}^2 + \boldsymbol{S}^2 + 2\boldsymbol{L}\cdot\boldsymbol{S}$$

(since $\boldsymbol{L}$ and $\boldsymbol{S}$ commute), so

$$\langle \boldsymbol{L}\cdot\boldsymbol{S}\rangle = \frac{1}{2}\left\langle (\boldsymbol{J}^2 - \boldsymbol{L}^2 - \boldsymbol{S}^2)\right\rangle = \frac{\hbar^2}{2}\Big(j(j+1) - l(l+1) - s(s+1)\Big)$$

This leads to this estimate for the magnitude of the spin-orbit interaction,

$$\langle H_{SO}\rangle = \frac{\beta}{2}(j(j+1) - l(l+1) - s(s+1)) \tag{19}$$

with, for an electron in an (n,ℓ) atomic orbital,

$$\beta = \frac{Z^4\hbar^4}{m^3c^2n^3a_0^4\ell(\ell+1)(\ell+1/2)} = \frac{Z^4 * 0.001447eV}{n^3\ell(\ell+1)(\ell+1/2)}.$$

Spin-orbit interactions are (being a relativistic effect) not large, but they lead to spectroscopically observable level splittings. The Z^4 - dependence (we say that larger nuclear charges $\Rightarrow$ higher velocities $\Rightarrow$ larger relativistic corrections) means that spin-orbit interactions are larger in metals, although they aren't insignificant in organic molecules. Since

the spin-orbit interaction allows mixing of the spin angular momentum and orbital angular momentum, it provides a mechanism for singlet-triplet conversions which has a dramatic effect on the dynamics of the evolution of excited spectroscopic states.

Appendix *L*

I. Newton used a configuration space to describe a mechanical system, a space with coordinates that described the positions of all the particles in the system. The dynamics was determined by a set of second order (in time) differential equations for the coordinates. W. R. Hamilton ($\sim$ 1833) introduced a description based on *phase space*: A system with f degrees of freedom is described with f coordinates $q_1, \ldots q_f$ and f momenta $p_1, \ldots, p_f$. In this space, the dynamics is fixed by a set of $2f$ first order (in time) differential equations

$$\dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i}; \qquad \dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i}, \quad i = 1, \ldots, f \tag{20}$$

generated by a function $\mathcal{H}(p_1, \ldots, p_f, q_1, \ldots, q_f) = \mathcal{H}(p, q)$. As a mathematical proposition, any system of f second order differential equations in time can be recast in the form (20). But, as there are many *canonical** formulations of the dynamics. It is this Hamiltonian formulation of dynamics that was used by the constructors of quantum mechanics. As a consequence, any classical relation involving p's and q's has a quantum mechanical analogue.

The center peice of Hamilton's formulation is the idea of a *canonical transformation*, of a transformation from one set of p's and q's with their $\mathcal{H}(p, q)$ to another set of P's and Q's with their $\mathcal{H}_2(P, Q)$. Time evolution $\sim p_i(0) \rightarrow p_i(t)$, $q_i(0) \rightarrow q_i(t)$, $i = 1, \ldots f$, is, for example, a canonical transformation. This transformation is *generated* by the function $\mathcal{H}(p, q)$ using (20). In the same sense, linear transformations (spatial displacements) of a system are generated by the total linear momentum of the system and rotations are generated by the total angular momentum of the system. So it was known at the outset that there would be quantum mechanical analogs of these relations.

* definitions of p's and q's and an associated function $\mathcal{H}(p, q)$ for which (20) describes the dynamics of the system.

Appendix *W*

The electromagnetic field provided the first *interactions* between particles that satisfied the rules of special relativity.

How does one construct the Hamiltonian for a particle that is moving in the pressence of an electromagnetic field? The *canonical* construction proceeds this way:

1° Express the field in terms of the four component electromagnetic potential $\{\boldsymbol{A}(\boldsymbol{r},t), \phi(\boldsymbol{r},t)/c\}$. $\boldsymbol{A}(\boldsymbol{r},t)$ is the *vector potential* that generates the magnetic field

$$\boldsymbol{B}(\boldsymbol{r},t) = \nabla \times \boldsymbol{A}(\boldsymbol{r},t)$$

and $\phi(\boldsymbol{r},t)$ is the *electrostatic potential* that generates the electric field

$$\boldsymbol{E}(\boldsymbol{r},t) = -\nabla\phi(\boldsymbol{r},t) - \frac{\partial \boldsymbol{A}(\boldsymbol{r},t)}{\partial t}.$$

2° These fields, of course, can be determined by solving the *field equations*

$$\begin{aligned} \left[\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right] A(\boldsymbol{r},t) &= -\boldsymbol{j}(\boldsymbol{r},t)\,\mu_0 \\ \left[\nabla^2 - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right] \phi(\boldsymbol{r},t) &= -q(\boldsymbol{r},t)/\epsilon_0 \\ \nabla\cdot\boldsymbol{A}(\boldsymbol{r},t) + \frac{1}{c^2}\frac{\partial\phi(\boldsymbol{r},t)}{\partial t} &= 0 \end{aligned} \qquad (21, SI)$$

with the current density, charge density $\{\boldsymbol{j}(\boldsymbol{r},t),\ q(\boldsymbol{r},t)\,c\}$ the *source* of the field (a four-vector, of course). μ_0 and ϵ_0 are constants introduced in the SI system of units. The fifth relation in (21) enforces the *Lorentz* guage.

3° If $H(\boldsymbol{p},\boldsymbol{r})$ is the Hamiltonian for a particle in the absence of an electromagnetic field, then the Hamiltonian for this particle in the presence of the electromagnetic field will be (if the particle has charge q) $H(\boldsymbol{p} + q\,\boldsymbol{A}(\boldsymbol{r},t), \boldsymbol{r}) + q\,\phi(\boldsymbol{r},t)$.

In a quantal description of a system, of course, H, $\boldsymbol{A}$ and ϕ all become operators.

When Dirac executed this program with his Lorentz invariant formulation, he found that additional energy terms (associated with the fact that the state vector had four components) appeared. One of these terms was

$$\frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\nabla\times\boldsymbol{A}(\boldsymbol{r},t)=\frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\boldsymbol{B}(\boldsymbol{r},t)$$

with $\boldsymbol{\sigma}$ a 3D vector made out of the Pauli spin matrices (the spin *angular momentum* is $\hbar\times\boldsymbol{\sigma}$). This is the same expression that a classical E & M calculation would associate with a particle that had a magnetic moment

$$\boldsymbol{\mu}=-\frac{e\hbar}{2m}\boldsymbol{\sigma}=-\frac{e}{m}\boldsymbol{s} \qquad (22,SI)$$

In classical E & M, a current I flowing around an area A will give rise to a *magnetic moment* that is perpindicular (in the "right hand rule" direction) to the area with magnitude $I\cdot A$.

In general, a particle with mass m and charge q moving in a circular loop with angular momentum $\boldsymbol{L}$ will have a magnetic moment

$$\boldsymbol{M}=\frac{q}{2m}\boldsymbol{L}. \qquad (23,SI)$$

proportional to the angular momentum of the particle. For an electron in an atomic orbital with orbital angular momentum $\boldsymbol{\ell}$ the magnetic moment will be

$$\boldsymbol{m}=\frac{-e}{2m_e}\boldsymbol{\ell}$$

a quantity with magnitude

$$|\boldsymbol{m}|=\frac{e\hbar}{2m}\sqrt{\ell(\ell+1)}$$

The basic unit of the magnetic moment here is the Bohr magneton (the magnetic moment of an electron in a $2p$ orbital of the Bohr model)

$$\beta=\frac{e\hbar}{2m}$$

In fact, (22) associates a magnetic moment of one Bohr magneton with the spin of the electron. This means that the spin magnetic moment is twice that which would have been

assigned on the basis of the associated angular momentum. This *anomalous* behavior is generally described by saying that the magnetic moment of the electron is

$$\boldsymbol{\mu} = \beta g \left(1 + \frac{\alpha}{2\pi} + \cdots\right).$$